Time aberrations of uniform fields: An improved reflectron mass spectrometer for an atom-probe field-ion microscope

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(Received 7 July 1993; accepted for publication 8 August 1993)

The mass resolution of the atom-probe field-ion microscope is limited by the time resolution of the ion-separating spectrometer. Time aberrations of uniform fields are investigated in general in order to characterize the optimal performance of high-transmission, high-mass resolution, multistage reflectron lenses. Correction of higher order time aberrations greatly improves the mass resolution. For an ion beam with an energy distributed uniformly about some nominal energy, $E_0 \pm dE$, mass resolutions (base width) of $m/\Delta m = 848, 1344, 2151, 3571$ can be achieved for single-, double-, triple- and quadruple-stage reflectron mass spectrometers when $dE = 0.1E_0$. A unique design example employing both second- and third order time correction is given for an atom-probe field-ion microscope.

I. INTRODUCTION

The atom-probe field-ion microscope is a unique instrument for the characterization of microstructure on an atomic scale. This point projection microscope allows one to observe individual atoms in direct lattice space on the surface of a sharply pointed tip, with a radius of 5–50 nm, and to determine the chemical identities, that is, the mass-to-charge state ratio of preselected individual atoms via time-of-flight mass spectroscopy. Figure 1 is a schematic diagram of an atom-probe field-ion microscope based on a reflectron time-of-flight mass spectrometer. Individual atoms on the surface of the field-ion microscope (FIM) specimen are imaged with the aid of an imaging gas, typically helium or neon, via the mechanism of field ionization. Helium atoms are ionized, above individual atoms on the surface of the tip, as a result of electrons tunneling from the He atoms into the specimen at a local electric field of 45–50 V nm$^{-1}$. A FIM specimen is typically maintained at a voltage in the range 5–20 kV dc with the aid of a field-ionization threshold fields. The resulting positively charged helium ion is then repelled from the site of a field-evaporation event and its detection one nanosecond after the field-evaporation pulse is picked off and used to start a digital timer; this pulse initiates the field-evaporation process. The digital timer is stopped when an ion arrives at the chevron detector (Fig. 1); the latter consists of two-channel electron multiplier arrays in series that has a gain of greater than $10^6$ for a single ion. The entire process of initiating the field-evaporation pulse, recording the values of the steady-state and field-evaporation voltages, recording the time-of-flight values measured by the digital timer, and calculating the mass-to-charge state ratios is accomplished with the aid of a computer. Since the time-of-flight is proportional to the square root of the mass-to-charge state ratio, by measuring the time-of-flight between the initiation of a field-evaporation event and its detection one can determine the mass-to-charge state ratio of each field-evaporated ion. Any residual time aberrations in the spectrometer tend to smear out the time signature of the field-
II. ION OPTICS

Of the many approaches available to achieve high-resolution time filtering of an electron or ion beam, the reflectron lens is perhaps the simplest and most elegant. The principle of the reflectron spectrometer exploits the symmetry of charged particle trajectories following parabolic paths in the retarding (mirror) uniform fields of the lens. Simply, particles with more energy penetrate more deeply into the mirror lens field, and hence spend more time in completing their parabolic trajectories. By carefully selecting the distance that the particle drifts before entering the retarding lens fields, and matching the magnitude of the mirror retarding field for the preselected drift distance, time compensation can be achieved. The degree of time compensation will in general depend upon the intrinsic energy spread of the charged particle beam, and the number of reflectron stages employed in the lens itself. We present here a simple, yet general, method to design a reflectron lens with a given time (mass) resolution.

Assume that an ion of mass $m$, charge $q$, and energy $E$ originates at a source. As applied to the goals of the present paper, this source is the tip of a FIM and the energy of the ion is characteristic of the energy required for its field evaporation. The ions subsequently follow trajectories through a reflectron time-of-flight spectrometer. The total drift distance outside of the reflectron lens is $L$ which can arbitrarily be divided into an entrance drift distance $L_1$ and an exit drift distance $L_2$ (Fig. 2). In the ensuing analysis, assume that the ion path is perpendicular to the entrance electrode of an $n$-stage reflectron lens, with the understanding that the reflectron lens does not focus in the transverse direction (Fig. 2). The time aberrations of the reflectron lens can be more directly accessed by assuming that an ion of energy $E$ results from an acceleration across a potential $V(E=qV)$. The distribution of energies about the nominal energy, $E_0 \pm dE$, can similarly be characterized by the acceleration voltage $V_0 \pm dV = V_0(1 \pm \delta)$. Here, the distribution of acceleration potentials results from the field-evaporation pulse, the local variability in the threshold fields, and any screening of the tip by the first ions that are extracted by the field pulse. If each successive stage (uniform field region) in the reflectron has length $d_i$, and associated potential $V_i$, as shown in Fig. 2, the total transit time from source to detector is given by Eq. (1):

$$t = t_{\text{drift}} + \sum_{k=1}^{n-1} t_k + t_n$$

$$= \frac{L}{\sqrt{2qV_0/m}} \left[ \frac{1}{1 \pm \delta} \right]$$

$$+ \frac{L}{\sqrt{2qV_0/m}} \left[ \sum_{i=1}^{n-1} 4 \frac{d_i}{V_i} \left( \sqrt{1 \pm \delta - \frac{1}{V_0} \sum_{j=1}^{n-1} V_j} \right) - \sqrt{1 \pm \delta - \frac{1}{V_0} \sum_{j=1}^{n-1} V_j} \right]$$

$$+ \frac{L}{\sqrt{2qV_0/m}} \left[ 4 \frac{d_n}{V_n} \left( \sqrt{1 \pm \delta - \frac{1}{V_0} \sum_{j=1}^{n-1} V_j} \right) - \sqrt{1 \pm \delta - \frac{1}{V_0} \sum_{j=1}^{n-1} V_j} \right]. \quad (1)$$

The first term is the time spent in the drift region (both $L_1$ and $L_2$), $t_{\text{drift}}$. The sum in the second term accounts for the time spent in all $n-1$ predeceleration stages $t_k$, and the
final term accounts for the transit time in the turn-around or mirror region in the nth reflectron stage, $t_n$. The time deviation for the entire ion trajectory due to energy dispersion in the initial beam can be characterized in the charged particle formalism by deriving the time aberrations for the reflectron lens. The aberration coefficients are typically extracted from a series expansion of the variable of interest in powers of the freely varying parameter. In this case, we expand the transit time as a function of the ion's initial energy deviation. Specifically,

$$t = \sum_{k=0}^{\infty} \frac{T_k}{k!} \delta^k$$

$$= t_0 + T_1 \delta + T_2 \delta^2 + T_3 \delta^3$$

$$= t_0 + \sum_{k=1}^{\infty} T_k \delta^k,$$  

(2)

where the coefficients, $T_k$, $k=1,2,3...$, in Eq. (2) are the time-aberration coefficients of order $k$ and $\delta$ is the relative energy (voltage) deviation, $dE/E_o(dV/V_o)$. The nominal transit time for ion beams with energy $E_o$ is given by $t_0$. When $\delta$ is large, and the $T_k$ are nonzero, there can be considerable time spreading of the ion beam as it passes through the reflectron lens. In order to improve the time resolution of the reflectron lens, the time aberration coefficients $T_k$ must be minimized. Mamyrin and co-workers have shown that considerable improvement in the time resolution is possible by finding the appropriate strengths of the uniform fields for first- and second-order aberration corrections. We generalize this process here in order to correct the highest order time aberrations in order to achieve a fixed mass resolution in systems where the energy dispersion in the initial beam is large, such as in an atom-probe, time-of-flight experiment; this is particularly the case where the pulsed-field evaporation is accomplished using an electric field.

An $n$-stage time-of-flight reflectron lens is required to eliminate the time aberration coefficients, $T_k$, to order $n$. A set of $n$-linear equations is formed, where the matrix equation is given explicitly in terms of the derivatives

$$
\begin{bmatrix}
\frac{\partial t}{\partial \delta} \\
\frac{\partial^2 t}{\partial \delta^2} \\
\frac{\partial^3 t}{\partial \delta^3} \\
\vdots
\end{bmatrix} =
\begin{bmatrix}
\frac{\partial t_1}{\partial \delta} \\
\frac{\partial^2 t_1}{\partial \delta^2} \\
\frac{\partial^3 t_1}{\partial \delta^3} \\
\vdots
\end{bmatrix}
\begin{bmatrix}
\frac{d_1}{L} \\
\frac{d_2}{L} \\
\frac{d_3}{L} \\
\vdots
\end{bmatrix}
$$

(3)

(with respect to the voltage [energy] deviations in the incident beam) of the time spent in each reflectron stage and derivatives of the drift time. This set of equations can be solved for the normalized electrode spacing, $d/L$, for given reflectron potentials, $V_k$, thereby eliminating the time aberrations up to order $n$. The figures of merit for a corrected reflectron are the relative time deviation, and mass resolution:

$$\frac{dt}{t_0} = \frac{(t-t_0)}{t_0},$$

(4)

and

$$\frac{m}{dm} = \frac{t_0}{2(t-t_0)}.$$  

(5)

For a single-stage reflectron, there is a unique solution which requires that the ion spend exactly half the (total transit) time in the drift space and half the time in the reflectron mirror itself. For a multistage reflectron, there are an infinite number of possible solutions to reduce the time aberrations (up to order $n$) to zero given the continuous distribution of possible electrode potentials on each reflectron stage. The optimum solution is found for a given $n$-stage reflectron design by evaluating the mass resolution for each solution to Eq. (3), and retaining only the best design. For example, in the two-stage reflectron design, no second-order corrected solutions exist when the first-stage deceleration potential is reduced below $2V_o/3$. A continuous set of solutions exists when $2V_o/3 < V_1 < V_o$. Kararaev et al. found the optimum solution at $V_1=2V_o/3$ and proposed alternative designs, close to the optimum in later publications. In order to eliminate higher order time aberration coefficients, the three- and four-stage designs must have the first-stage deceleration potentials (approximately) larger than $V_1 > 0.79V_o$ and $V_1 > 0.83V_o$, respectively.

The performance of the time-of-flight $n$-stage reflectron lens is summarized in Fig. 3. The time deviation [Eq. (4)] is shown as a function of the energy deviation, $\delta = dV/V_o$. The straight time of flight spectrometer (zero-stage reflectron) is not shown in this figure, but would appear as a nearly vertical line. The curves shown in Fig. 3 result from the solution of Eq. (3) and the all-orders ex-
pression for time. The analytic solutions for the time deviations were confirmed by numerical ray tracing using a modified Adams–Moulton predictor corrector method. It is evident that the odd-order (odd number of reflectron stages) solutions, that have dominant even order aberrations, are characterized by time-deviation curves that are even in energy deviation. The even-order (even number of reflectron stages) solutions have dominant higher order aberrations odd in the energy deviation. The odd-order designs are intrinsically better since ions with energies differing from the nominal energy will always be trailing in time, rather than being distributed both before and after the arrival of the nominal energy ion. The advantage of utilizing more reflectron stages is evident in Fig. 3. Eliminating higher order time aberrations increases the region of low time deviation at larger energy dispersion, as expected. In general, the time deviation curves are not symmetric about $dV/V_o=0$. The single-stage reflectron nearly has this symmetry. The asymmetry in the time deviation curves indicates that the optimum operating condition for a reflectron depends in detail on the energy distribution of the incident ion beam.

The (absolute value) of the mass resolution is shown as a function of the energy deviation in Fig. 4. The resolution is infinite when $dV/V_o=0$, hence curves were not computed for values less than $dV/V_o=0.01$. The mass resolution curves are also asymmetric about $dV/V_o=0$. Higher order solutions have higher mass resolution as expected. If the time aberration expansion in Eq. (2) is truncated such that only the next higher order uncorrected time aberration coefficient is retained when computing the mass resolution, erroneous results are found for large energy deviations, as shown in Fig. 5. When more reflectron stages are added, and higher order time aberrations are eliminated, each subsequent uncorrected aberration coefficient assumes a larger value. Since the contributions to higher order aberrations alternate in sign, as shown explicitly by the results in Fig. 3, erroneous design values for the mass resolution result unless the all order transit time is computed. For example, Fig. 5 predicts that using the first nonvanishing aberration coefficient from Eq. (2), that the quadruple-stage reflectron has a lower mass resolution than a triple-stage design for energy deviations greater than 10%. This is a result of prematurely truncating the time aberration series expansion.

For an ion beam with an energy distributed uniformly about some nominal energy, $E_o \pm dE$, mass resolutions (base width) of $m/dm=848, 1344, 2151, 3571$ can be achieved for single-, double-, triple-, and quadruple-stage reflectron mass spectrometers when $dE=0.1E_o$. These results represent significant improvements over conventional single-stage designs. These results also compare quite favorably with a 40-mrad acceptance angle Poschenrieder spectrometer. A Poschenrieder or toroidal spectrometer is a difficult lens to fabricate. Its mass resolution ($m/dm$) depends upon the acceptance angle employed with smaller acceptance angles yielding larger mass resolution values, $m/dm$, and smaller transmission. In contrast, the reflectron mass resolution, $m/dm$, depends upon the number of deceleration stages (and meshes) employed. The transparency (see Sec. III) of the reflectron meshes ultimately determine the transmission of the device as a whole.

Pulsed-laser atom probes (PLAPs) have been constructed in order to improve the mass resolution and to study insulating materials. A laser pulse induces field evaporation or desorption as a result of heating a FIM tip. The energy spread of such ions is approximately $kT$, where $k$ is Boltzmann’s constant and $T$ is temperature, or less than 0.1 eV. Thus the energy spread is negligible compared to the spread that occurs when employing pulsed electric fields to field evaporate ions. A PLAP has been constructed with an $m/dm$ of $(1 \times 10^3)$ flying a straight time-of-flight tube with a flight path of 7780 mm. Figure 4 demonstrates that for a double- or triple-stage reflectron
and an energy deviation of -0.02, the values of $m/dm$ are approximately $2 \times 10^5$ and $1.5 \times 10^6$, respectively. Thus employing a PLAP with a reflectron lens it should be possible to obtain an $m/dm$ value that is much greater than for one with a straight time-of-flight tube; in addition, a PLAP with a reflectron is considerably more compact than one with a straight TOF tube.

III. ATOM-PROBE FIELD-ION MICROSCOPE TIME-OF-FLIGHT SPECTROMETER DESIGN

Consider a design example for an atom probe with the capability of separating Pt isotopes ($Pt_{194}^+$ at 32.9% abundance; $Pt_{192}^+$ at 33.8% abundance; $Pt_{190}^+$ at 25.3% abundance) and the ability to distinguish Pt from Au (have enough mass resolution to separate $Pt_{196}^+$ from $Au_{197}^+$) at nominal acceleration potentials as high as 20 kV, with a relative energy dispersion in the field-evaporated source beam of ±10%. The Au ion isotopes accelerated by identical potential differences are distributed in time due to their different masses resulting in $dt/t \lesssim 2.52 \times 10^{-4}$. The lower limit on the size of the reflectron analyzer is determined by the timing resolution of the entire system. If the detection electronics' time resolution is 10 ns, then $q/m$ peaks which are separated by 30 ns and confined to ±5 ns of the nominal time are easily distinguishable. If the total drift distance is 1200 mm and the nominal ion beam energy is 20 keV, then the transit time for a 197 amu ion through the double- or triple-stage reflector time-of-flight spectrometers (including the necessary drift space) is 11.328 or 11.068 μs, respectively. Isotope peaks near mass 196 amu are separated by about 29 ns. The required time resolution of the spectrometer is ±5 ns, thereby requiring $dt/t = ± 4.3 \times 10^{-4}$ or $± 4.5 \times 10^{-4}$ for the two- or three-stage designs, respectively. Analysis of Fig. 3 indicates that the double-stage design barely meets the criteria for ±10% energy deviations, while the three-stage design easily meets the necessary resolution requirements. The benefit of longer drift distances (longer times) must be balanced against ease of construction, use and alignment, and the detrimental effects of stray fields. We choose a reflectron drift distance of 1200 mm.

Since no third-order aberration corrected designs have been implemented to date, the present design is configured to incorporate both second-order or third-order correction within a single instrument. In this way a direct comparison of the time aberrations can be made. With the minimum drift distance fixed by the sampling resolution, and the optimum reflectron potential ranges determined from the solution to Eq. (3), the individual reflector field stage lengths, $d_i$, need only be matched, i.e., $d_i$(two stage) = $d_i$(three stage), and $d_i$(two stage) = $d_i$(three stage) + $d_i$(three stage). Additionally, $d_i$(three stage) should be an integral multiple of the distance between subsequent aperture electrodes in the mirror region of the two-stage design. The results of the two compatible designs are summarized in Table I.

A schematic cross section of the dual double-stage/triple-stage reflector is shown in Fig. 6 with trajectories for $H^+$ at 11.7, 13.0, and 14.3 keV (±10% energy deviation). The total length of the reflectron lens is 103.47 mm, and the interelectrode spacing in the mirror region is 5.908 mm. The inner diameter of the uniformly spaced electrodes is 60 mm. The longer electrodes shown in the figure are the positions of the required wire-mesh screen that insure field uniformity. For three meshes with 90% transmission, the entire system provides about 50% transmission. The entrance beam size is limited to a 5 mm diameter and an angular divergence of ±1°. The beam nominally enters the lens at the entrance 6.03 mm from the reflectron optical axis at an angle of 1.68° or 1.99° for the two-stage or three-stage design, respectively. Thus, a secondary set of deflectors is required to accommodate both designs simultaneously. This design should achieve mass resolutions of roughly 1300 or 2100 for ±10% energy deviations in the two-stage or three-stage designs, respectively. In conclusion, an all orders time-aberration correction scheme was given for the design of reflectron time-of-flight mass spectrometers with high transmission and high-mass resolution. An improvement of over 300% (in mass resolution) can be obtained by utilizing a triple-stage as opposed to a single-stage reflector lens in an atom-probe field-ion microscope system where the energy distribution in the field-evaporated beams is intrinsically large ($dE = ± 0.1 E_0$).

### Table I. Design summary of parameters specifying the dual two-stage/three-stage reflectron design. $L = 1200$ mm and the interelectrode spacing in the mirror region is 5.908 mm.

<table>
<thead>
<tr>
<th>Design</th>
<th>$d_i/L$</th>
<th>$d_i/L$</th>
<th>$d_i/L$</th>
<th>$V_i/V_o$</th>
<th>$V_i/V_o$</th>
<th>$V_i/V_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.00250</td>
<td>0.08371</td>
<td>-</td>
<td>0.67000</td>
<td>0.57649</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>0.00950</td>
<td>0.00985</td>
<td>0.00736</td>
<td>0.79470</td>
<td>0.01580</td>
<td>0.54698</td>
</tr>
</tbody>
</table>

FIG. 6. A schematic cross section of the dual double-stage/triple-stage reflectron with trajectories for $H^+$ at 11.7, 13.0, and 14.3 keV (±10% energy deviation). The total length of the reflectron lens is 103.47 mm, and the interelectrode spacing in the mirror region is 5.908 mm.
ACKNOWLEDGMENTS

We would like to thank Dr. G. G. Hembree, Dr. G. van Bakel, Dr. J. C. H. Spence, and W. Qian for useful discussions. This work was supported in part by NSF Grant No. DMR91-12550 (MRS), and NGS Grant No. DMR89-19073, and DMR91-21635 (DNS).

22Buckmee-Mears Corporation, 89% transmission for model MC-49.